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Nano Silica Melamine Trisulfonic Acid as an Efficient and Reusable Heterogeneous Catalyst for the Synthesis of 5-Substituted-1*H*-Tetrazoles

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A convenient method for the synthesis of 5-substituted-1*H*-tetrazoles from organic nitriles and sodium azide in the presence of nano silica melamine trisulfonic acid is reported. A series of aliphatic and aromatic nitriles underwent a [3+2] cycloaddition with sodium azide to afford tetrazoles in good to excellent yields and acceptable reaction times. The nano silica melamine trisulfonic acid is an efficient heterogeneous nanocatalyst with high catalytic performance. The nano silica melamine trisulfonic acid is readily prepared, environmentally friendly and reusable. The catalyst was characterized by powder X-ray diffraction, energy-dispersive X-ray mapping and SEM techniques. This simple and cost effective procedure could be promising for further applications in organic syntheses.

Keywords: Nano silica melamine trisulfonic acid, Tetrazole, Heterogeneous nanocatalyst, Cycloaddition, Sodium azide

INTRODUCTION

Tetrazoles are an important class of nitrogen-rich heterocycles with a wide range of applications in organic synthesis, coordination and medicinal chemistry [1-3]. They are extensively used in herbicides and fungicides, material sciences and nanostructured compounds [4-6]. Tetrazoles have also been frequently used as the stabilizers in photography [7]. The nitrogen content of tetrazoles is 80%, which is the largest percentage among the heterocyclic compounds. So, tetrazoles and their derivatives have been explored as the main constituents in various explosives and propellant compounds [7]. Tetrazoles were synthesized for the first time in 1885, by J. A. Bladin [8]. Since then, many attempts have been made to develop more efficient and eco-friendly methods for the construction of tetrazole frameworks [9,10].

Catalytic technologies played a vital role in the economic development in chemical industries in 20th century [11]. Historically, mineral liquid acids have been extensively used in acid catalyzed organic reactions. Serious corrosiveness, poor recyclability, tedious neutralization and separation processes, resulting hazardous wastes, in addition to the high toxicity of mineral liquid acids have greatly limited their applications in modern chemical industries [12-14]. Therefore, in terms of green chemistry, there is an essential need for replacement of homogeneous liquid acids by more cleaner heterogeneous solid acid catalysts [15]. Typically, heterogeneous catalysts offer several useful benefits over their homogeneous counter parts, such as good catalytic activities, high efficiency and selectivity, reusability, easy separation from the reaction mixture, reductive corrosion, and also more environmentally impacts from the green chemistry standpoints [16,17]. However, a major obstacle to such progress is the lack of a solid acid that is as effective and inexpensive as sulfuric acid [13].

Organic-based materials containing sulfonic acids (-SO_3H) groups are especially attractive catalysts, due to high acidity and efficiency, in addition to their good stability. In recent years, heterogeneous catalysts, chiefly solid acids and those based on micelle-templated silica support and other mesoporous high surface area, play a critical role in acid-catalyzed chemical transformations [17-23]. When nano scale materials are selected for supporting, the dispersible capability of catalyst in solution is improved and acts like a pseudo-homogeneous catalyst. So, the

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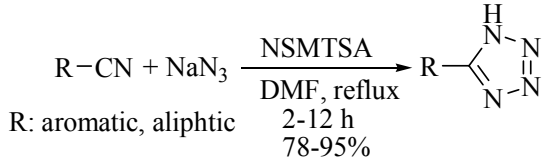
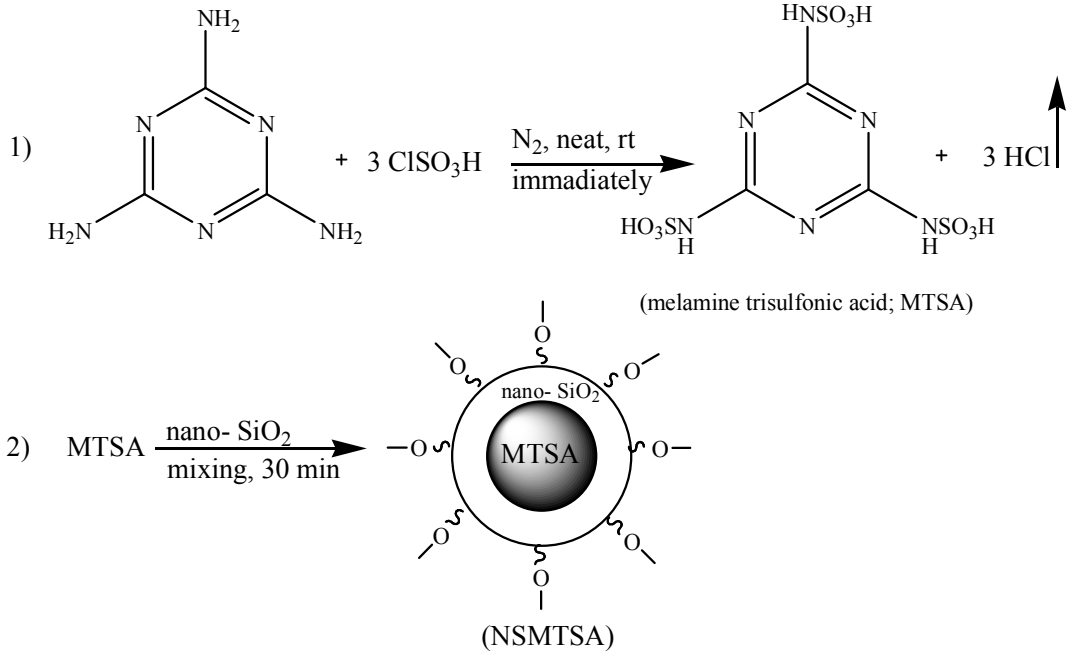


Scheme 1. Synthesis of 5-substituted-1*H*-tetrazoles from organic nitriles and sodium azide catalyzed by NSMTSA



Scheme 2. Preparation of NSMTSA from the reaction of melamine and chlorosulfonic acid and supporting on nano silica

diffusion rate of reactants to catalyst sites is increased and thus the reaction rate is enhanced dramatically [24,25]. It has been shown that the type of support material used is a critical factor in the performance of the resulting supported catalyst or reagent in an organic reaction system [11]. Among various supports for the preparation of solid acids, nano silica occupies a preeminent position because of its good stability, easy preparation and handling, well defined dimensions, availability, and simply functionalization.

Nowadays, there has been increasing publications by emphasis on environmentally friendly solid catalysts such as nanoZnO, nanoCuO, tetrabutylammonium hydrogen sulfate (TBAHS), Cu-MCM-41 nanoparticles, organoaluminum-azieds, CoY/zeolite, OSU-6, $Cu(OAc)_2$, NH_4OAc, $[Pd(OAc)_2]$ dabco/$ZnBr_2$, mesoporous ZnS, $CuSO_4.5H_2O$, $H_2SO_4@SiO_2$ to reduce the amount of toxic wastes and show a good catalytic performance [1-6,26-35]. The limitations of some of the reported methods are realized from their long reaction times, low yields, harsh reaction conditions, expensive, toxic and stringent metal catalysts which needs tedious efforts to prepare them.

On continuation of our research studies on using and developing more efficient nano scale solid acid catalysts in organic synthesis [18,35,36], here, we report nano silica melamine trisulfonic acid (NSMTSA), as an efficient heterogeneous catalyst for the facile synthesis of 5-substituted-1*H*-tetrazoles from organic nitriles and sodium azide (Scheme 1).

Melamine is a cheap and commercially available reagent. Melamine reacts with neat chlorosulfonic acid under N_2 atmosphere at room temperature (Scheme 2). Because of the fast evaluation of HCl gas from the reaction vessel, no special workup procedure was needed and the reaction was readily access [37-39]. To support the melamine trisulfonic acid (MTSA) on the surface of nano-SiO_2 through formation of partial hydrogen bonding, the synthesized MTSA was physically mixed with nano silica. Thereby, nano silica melamine trisulfonic acid (NSMTSA) was produced (Scheme 2).

Characterization of NSMTSA by Instrumental Examination

The structure of the prepared NSMTSA was characterized by scanning electron microscopy (SEM), patterned X-ray powder diffraction (PXRD), energy-dispersive X-ray (EDX) mapping and Fourier transform infrared spectroscopy (FT-IR) techniques. SEM images of the particles showed spherical shaped morphology with an average particle size of about 65 nm (Fig. 1). Also, the presence and distribution of the N, C, Si, O, S atoms in catalyst structure is confirmed by EDX mapping (Fig. 2). To further explore, the chemically modification of the silica support with melamine trisulfonic acid particles was also studied by PXRD technique. Comparison between PXRD pattern of both nano silica and NSMTSA shows that two significant peaks are positioned at $2\theta = 22.005^{\circ}$ and 27.640°, which related to the presence of Si-O and S-O bonds in the crystalline structure of NSMTSA, respectively (Fig. 3).

In agreement with the FT-IR spectra, the bands centered at ~1658 and ~1513 cm^{-1} are related to the vibrational bending frequency of C=N and N-H bonds, respectively. The bands at ~589 and 1092 cm^{-1} are attributed to the Si-O-Si vibrations in NSMTSA catalyst. The asymmetric stretching vibration of O=S=O is also seen at ~1171 cm^{-1}. The very broad and intense O-H stretching absorption band appears in the region of 3329 cm^{-1} [37-40]. As clearly seen,

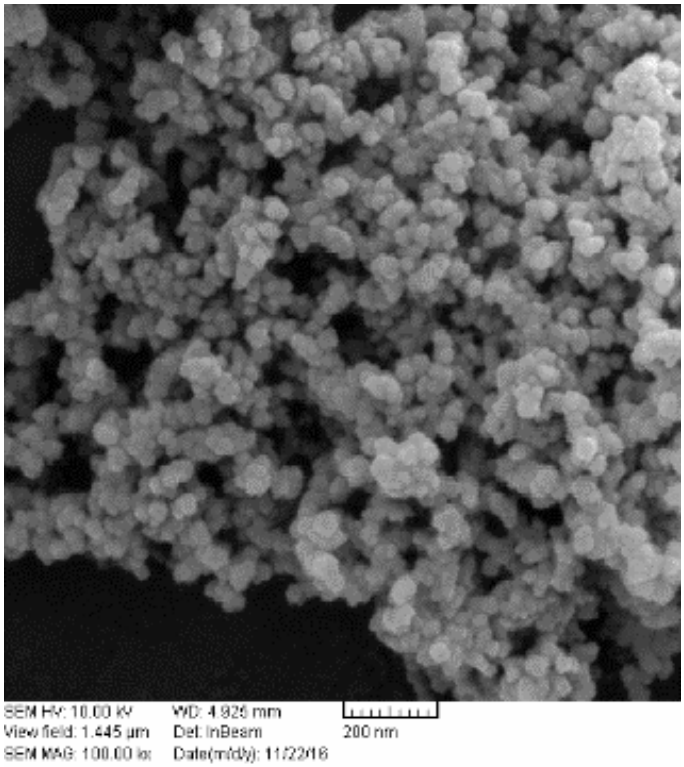
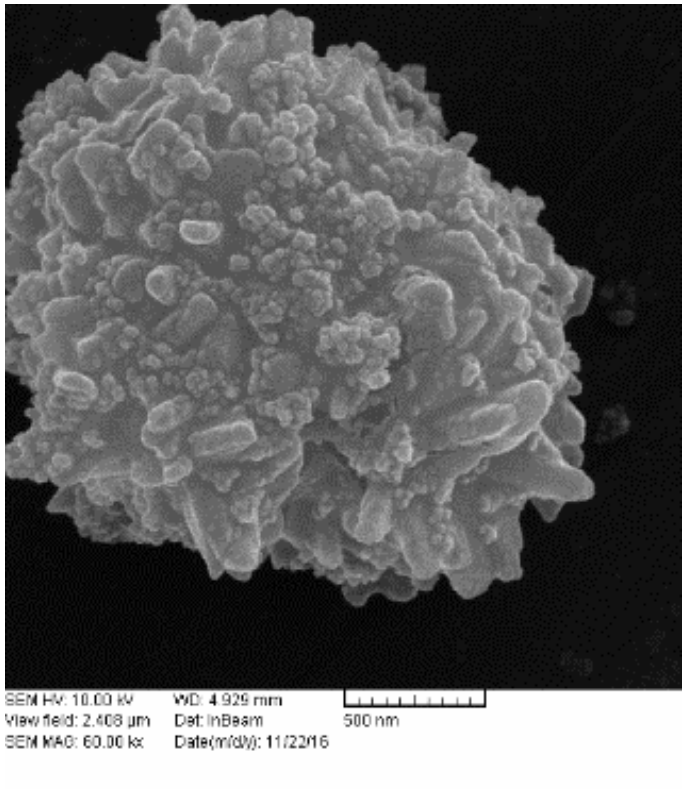


Fig. 1. SEM images of the prepared NSMTSA.



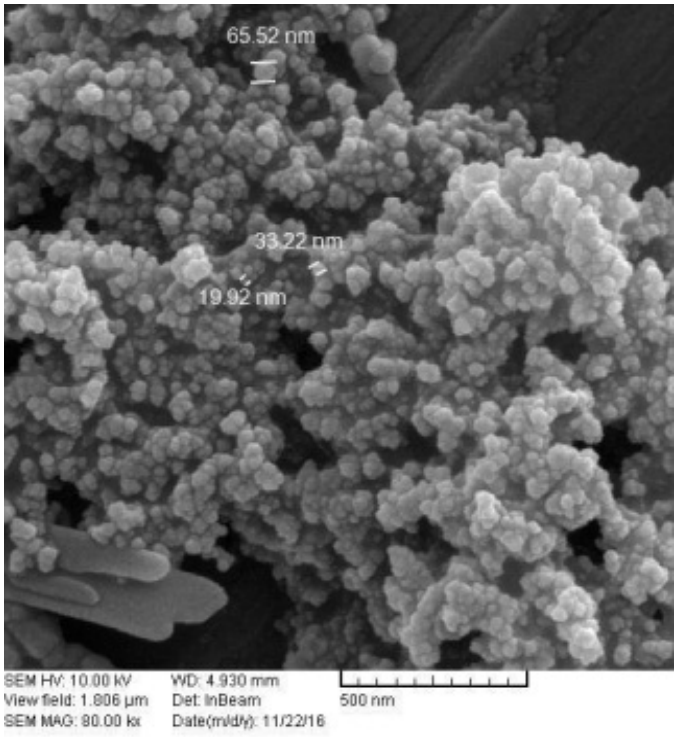


Fig. 1. Continued.

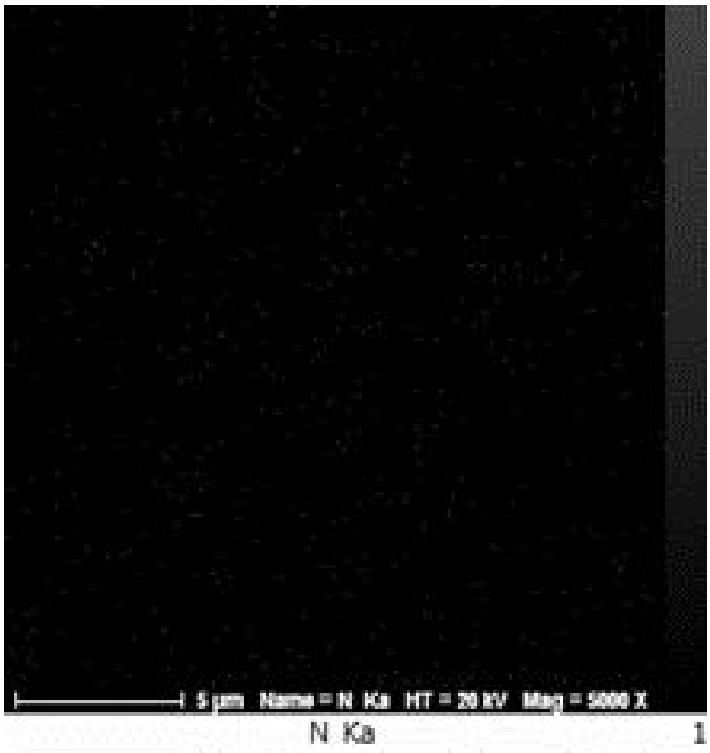
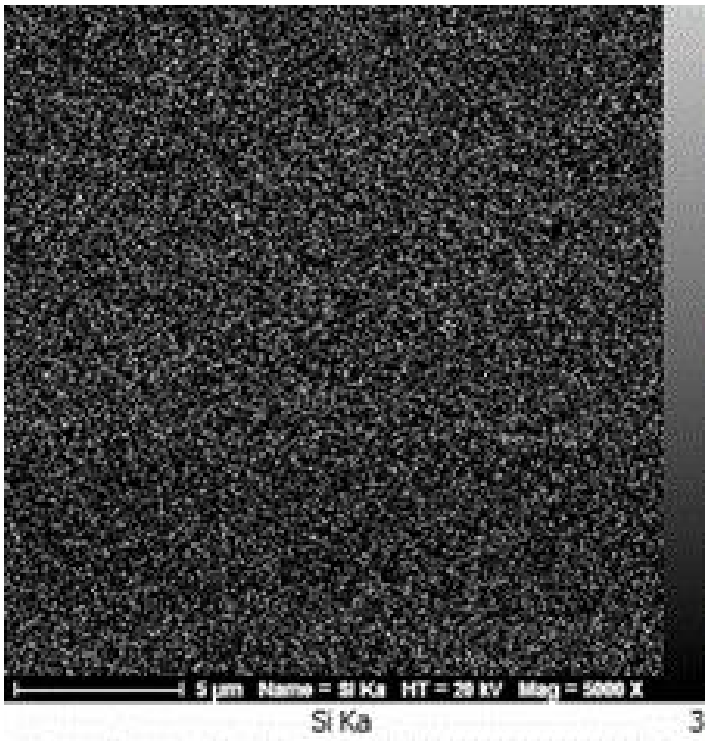


Fig. 2. EDX mapping results of the prepared NSMTSA.



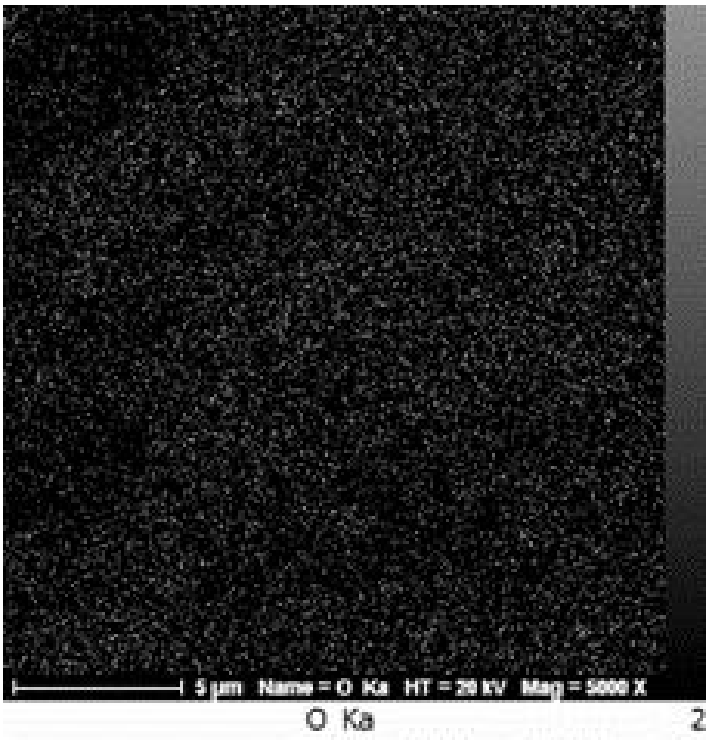
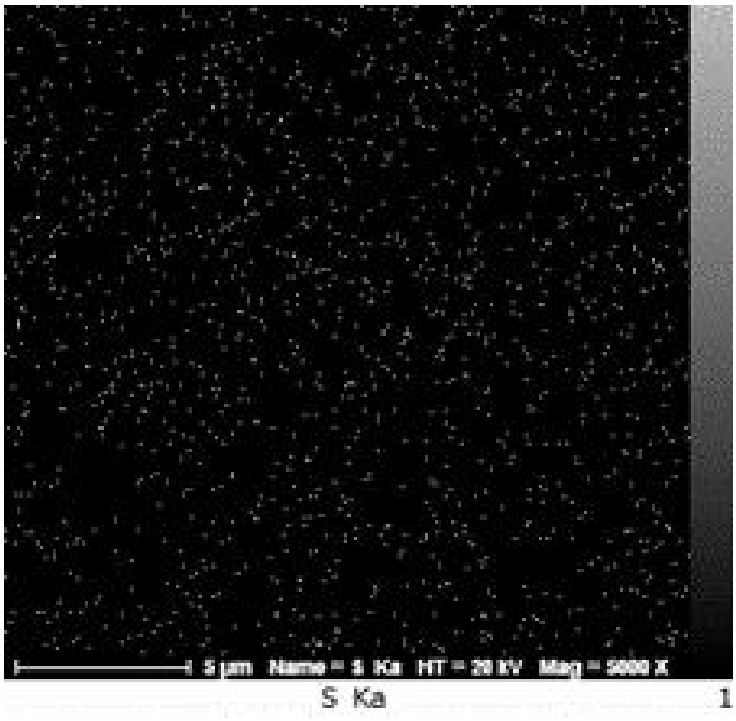


Fig. 2. Continued.



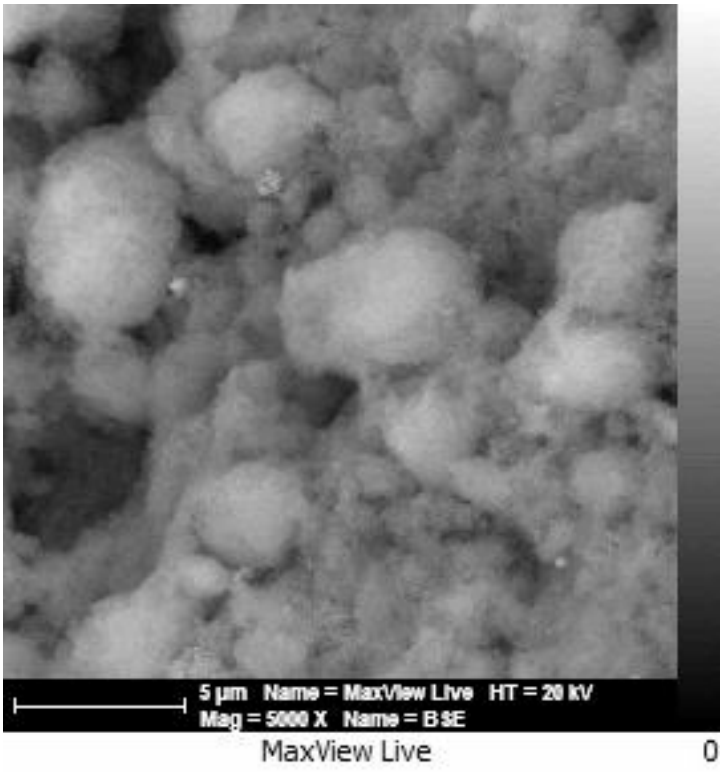


Fig. 2. Continued.

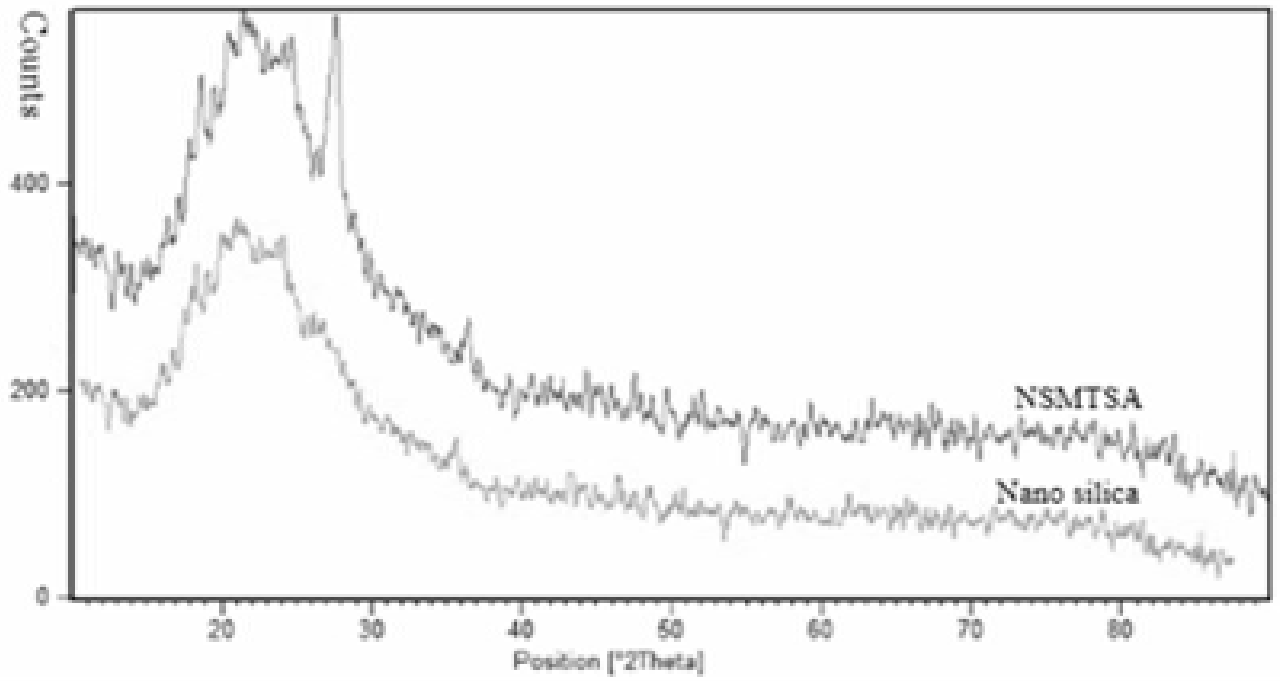


Fig. 3. PXRD pattern of the prepared NSMTSA and nano silica.

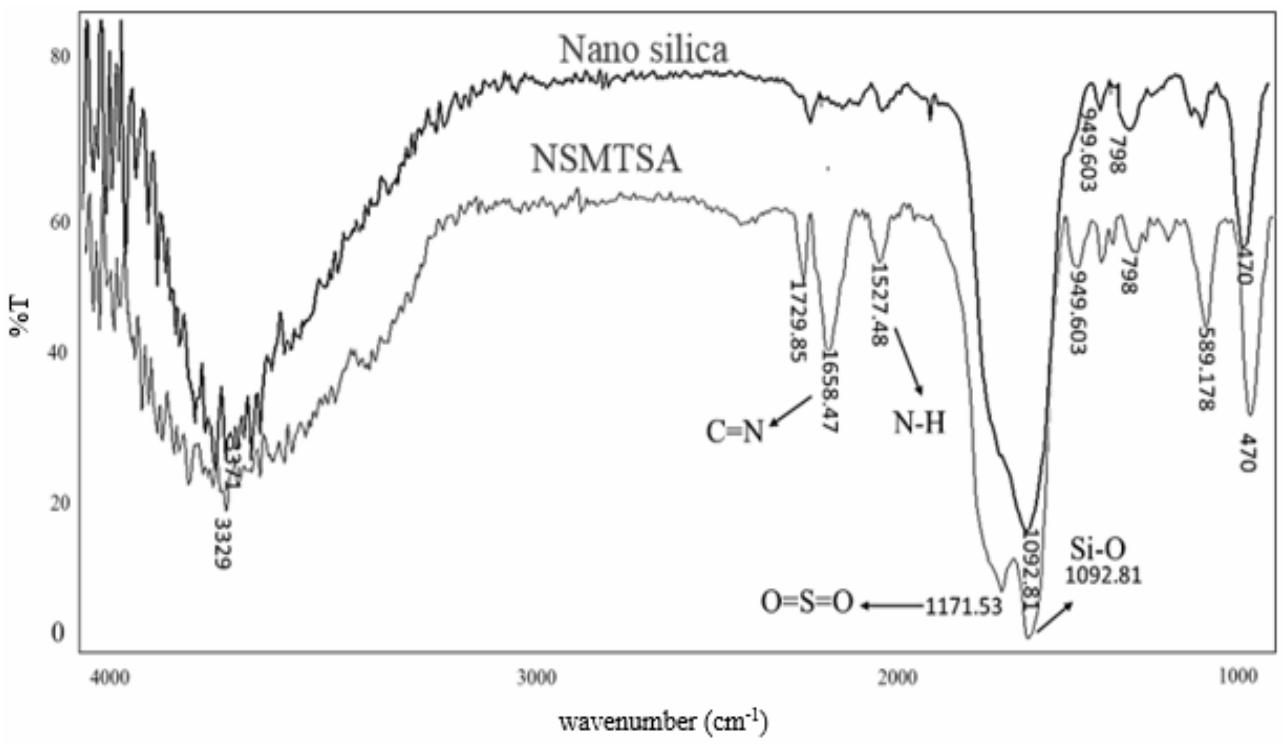


Fig. 4. FT-IR spectra of NSMTSA and nano silica.

the FT-IR spectrum gives a good indication of the successful preparation of NSMTSA (Fig. 4).

To optimize the reaction conditions, initially, the reaction of benzonitrile with sodium azide was selected as a model reaction. Therefore, to develop a better catalytic system, various reaction parameters such as solvent, catalytic loading and temperature were investigated.

To progress a reaction efficiently, the choice of an appropriate solvent is critical. Therefore, during our optimization studies, different types of solvents such as nonpolar, polar protic and polar aprotic solvents were examined (Table 1). Noticeably, the reaction was very sensitive to the type of solvent. No product was obtained in EtOH, MeOH, CH_3COOH, THF, toluene, CH_2Cl_2 and CH_3Cl (Table 1, entires 2-8). Other examined solvents such as H_2O and DMSO were effective, but gave lower yields than those obtained in DMF, even at longer reaction times. As shown in Table 1, among the various solvents studied, DMF was found to be the best. Hence, DMF was applied for all other reactions.

To evaluate the effect of catalyst loading on reaction rate, various amount of NSMTSA was examined (Table 2). It is clearly seen that NSMTSA plays an important role in [3+2] cycloaddition reaction of the benzonitrile with sodium azide. No product was obtained in the absence of NSMTSA (Table 1, entry 1). So, NSMTSA is considered to serve as an effective and promising catalyst in preparation of tetrazoles. On the basis of data in Table 2, when the amount of catalyst exceeds 3.4 mg, an increase in the yield of tetrazole formation occurs. Therefore, it is indicated that the optimum amount of NSMTSA is about 17 mg per 1 mol of benzonitrile under the adopted reaction condition (Table 2, entry 6). Lower conversions and longer reaction times were observed when the amount of catalyst used was 3.4-13.6 mg, whereas, further increase in the amount of catalyst, up to 24.8 mg, did not show any significant improvement in the yields of tetrazole formation.

Temperature was another important factor affecting the rate of reaction, which was also assessed. To study the effect of the temperature, the reaction was initially carried out at room temperature and then elevated to reflux condition. Notably, the reaction did not proceed at room temperature and no product was detected. So, in terms of times and yields, refluxing the reaction mixture in DMF was the best choice.

The possibility of recycling the NSMTSA was also examined using the reaction of benzonitrile with sodium azide under optimized conditions. After completion the reaction and during the isolating steps of product, the NSMTSA was separated from the reaction mixture by simple filtration. To remove any coordinate solvent and for assurance, the recycled catalyst before being subjected to another cycle of benzonitrile cycloaddition reaction, was put in an oven (at 100 °C for 2 h) and finally saved for the next run. Although the recycled catalyst was reused four times, a gradual decline in its catalytic activity and efficiency was observed. So, it can be considered as a weakly reusable catalyst (Table 3).

The scope and generality of this method was screened by applying the optimized reaction conditions in the [3+2] cycloaddition reaction of structurally wide range of aliphatic and aromatic nitriles with sodium azide in the presence of NSMTSA (Table 4).

EXPERIMENTAL SECTION

All chemicals were obtained from Merck, Aldrich and Fluka, and used as received without any further purification. IR Spectra (neat) were recorded on St-jean Baptist Ave Bomem 450 instrument. NMR spectra were recorded on Bruker Avance DPX (400 MHz) in $CDCl_3$ with TMS as an internal standard for protons and solvent signals as internal standard for carbon spectra. Chemical shift values are reported in δ (ppm) and coupling constants are given in Hz. The progress of all reactions was monitored by TLC on 2 × 5 cm pre-coated silica gel-60 F-254 plates of thickness of 0.25 mm (Merck). The chromatograms were visualized under UV 254-336 nm or by immersion in tanks of common chemical visualizer such as DNP, $H_2SO_{4(conc.)}$, I_2, *etc.*

Procedure for the Preparation of Nano silica Melamine Trisulfonic Acid; NSMTSA

A 250 ml suction flask charged with chlorosulfonic acid (75.2 mmol, 5 ml) was equipped with a gas inlet tube for conducting and neutralization of HCl gas overran adsorbing solution, ammonia. Melamine (25.07 mmol, 3.16 g) was added in small portions over a period of 30 min at room temperature under $N_{2(g)}$. HCl gas was evolved from the

Table 1. Screening the Various Solvents for the Reaction of Benzonitrile with Sodium Azide in the Presence of NSMTSA

Solvent	Time (h)	Yield (%)
H_2O	24	10
EtOH	24	N.R
MeOH	24	N.R
CH_3COOH	24	N.R
THF	24	N.R
toluene	24	N.R
CH_2Cl_2	24	N.R
CH_3Cl	24	N.R
DMF	6	92
DMSO	24	31

Table 2. Optimization of the Amount of NSMTSA for the Reaction of Benzonitrile with Sodium Azide in DMF

Catalyst (mg)	Time (h)	Yield (%)
None	24	N.R
3.4	15	40
6.8	12	48
10.2	10	83
13.6	8	75
17	6	92
21.4	6	88
24.8	6	86

reaction vessel, immadiately. After completion of the addition of melamine, the mixture was shaken for 60 min to ensure the outpouring the $HCl_{(g)}$. Meanwhile, the residual HCl was exhausted by suction. The mixture was triturated with CH_2Cl_2 (10 ml) and then filtrated.The solid residue was washed with CH_2Cl_2 (50 ml) and dried under vacuum. Melamine trisulfonic acid (7.6 g, 83%) was obtained as a white solid. Then, through the so-gel method, the prepared

Table 3. Recyclability of NSMTSA Catalyst in Cycloaddition Reaction of Benzonitrile with Sodium Azide

	Fresh	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Yield (%)[a]	92	90	88	85	82
Time (h)	6	6	6	6	6

[a]Isolated yield.

Table 4. NSMTSA Mediated Preparation of 5-Substituted-1*H*-tetrazoles in DMF under Reflux Conditions

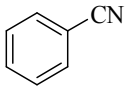
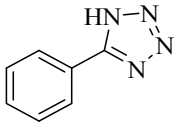
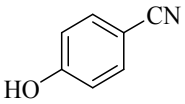
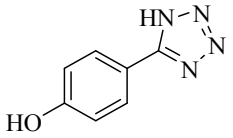
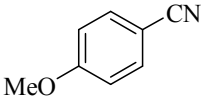
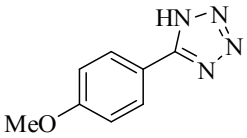
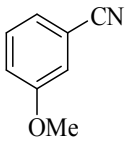
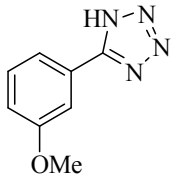
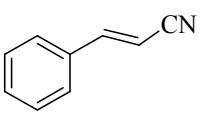
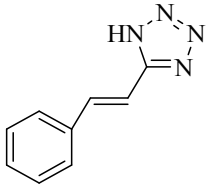
Entry	Nitrile	Tetrazole	Time (h)	Yield (%)[a]	M. p. (°C) (Lit. M.p.)[ref]
1			6	92	214-215(215-216) [34]
2			12	90	232-233(234-235) [8]
3			11	84	232-234(230-232) [35]
4			10.5	91	157-158(156-158) [34]
5			11	90	156-158(158-159) [35]

Table 4. Continued

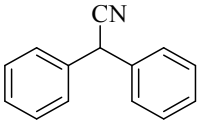
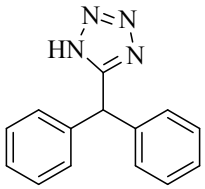
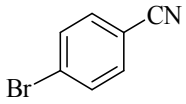
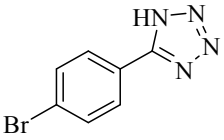
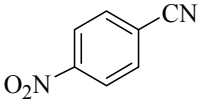
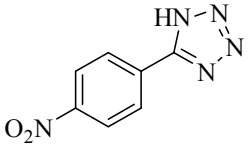
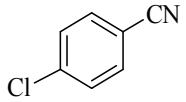
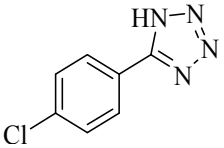
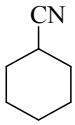
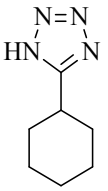
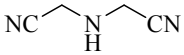
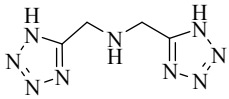
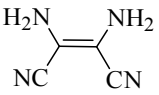
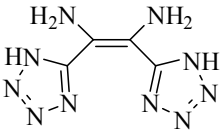
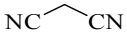
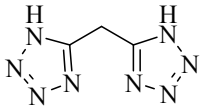
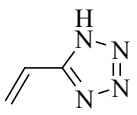
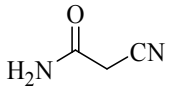
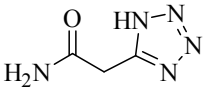
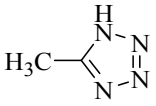
6			12	94	162-163(163-164) [35]
7			10	90	266-267(268-270) [34]
8			9	78	221-222(220-221) [8]
9			10	82	252-253(253-254) [35]
10			3	88	105-106(107-109) [35]
11			3	87	Oily [35]
12			6	93	Oily [35]
13			2	83	Oily [35]
14			4	89	Oily [35]

Table 4. Continued

15			3	95	Oily [35]
16	H_3C-CN		4	91	144-146(146-147) [35]

[a]Isolated yield.

nano silica gel (15 g) was added to the melamine trisulfonic acid (5 g) and stirred for 30 min. finally, the dried and grayish solid material obtained (20 g), was stored in a capped bottle (Scheme 2). m. p.: (melamine trisulfonic acid): 142-144 °C.

A Typical Procedure for the Synthesis of 5-Phenyl-1*H*-tetrazole

A mixture of benzonitrile (1 mmol, 0.103 g), sodium azide (1.5 mmol, 0.097 g), NSMTSA (17 mg), and DMF (5 ml) was taken in a 25 ml round-bottomed flask. The reaction mixture was refluxed 6 h. After completion the reaction, *i.e.*, disappearance of nitrile, monitored by TLC (n-hexane/EtOAc, 4:1, V/V), the reaction vessel was cooled to room temperature. To separate the catalyst, the mixture was centrifuged. The centrifugate was decanted and washed with ethyl acetate. To eliminate any unreacted nitrile, the mixture was treated 5 M HCl (15 ml) and then with ethyl acetate (30 ml) and stirred vigorously for 30 min. The resultant organic layer was extracted by n-hexane (3 × 50 ml) and washed with H_2O (2 × 50 ml) to omit the remainder of DMF. The solvent was dried by anhydrous $CaCl_2$ and evaporated by vacuo-rotary. A crude solid crystalline 5-phenyl-1*H*-tetrazole was obtained. To afford a pure tetrazole, column chromatography was performed using silica gel (100-200 mesh) eluting with petroleum ether/Et_2O mixture. 0.094 g of colorless crystals (92%, m. p.: 214-215 °C) was obtained (Table 4, entry 1).

The Spectral Data of Some of the Synthesized 5-Substituted-1*H*-tetrazoles

5-Phenyl-1*H*-tetrazole; (Entry 1, Table 4). White solid; m. p.: 214-215 °C; FT-IR (KBr, cm^{-1}): v 3235-2159 (N-H stretch.), 1608 (aromatic C=C stretch.), 1563 (N-H bending.), 1486 (C=N stretch.), 1410 (C-N stretch.), 1255 (N=N stretch.), 1164, 1056, 992 (Ring tetrazole and amine 2°), 695, 753; ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 16.85 (br, 1H, -NH), 8.1-8.06 (s, 2H, Ph), 7.69-7.63 (s, 3H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6, δ (ppm)): 155.88 (NH-C=N), 149.2, 131.12, 128.55, 125.06.

5-(4-Hydroxyphenyl)-1*H*-tetrazole; (Entry 2, Table 4). White solid; m. p.: 232-233 °C; FT-IR (KBr, cm^{-1}): v 3300 (O-H stretch.), 1611 (aromatic C=C stretch.), 1587 (N-H bending.), 1513 (C=N stretch.), 1414 (C-N stretch.), 1250 (N=N stretch.), 1187, 1109, 1032 (ring tetrazole and amine 2°); ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 16.45 (br, 1H, -NH), 10.27 (br, 1H, -OH), 7.91-7.80 (s, 2H, Ph), 6.92-6.87 (s, 2H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6, δ (ppm)): 160.47 (NH-C=N), 155.32, 129.4, 116.63, 115.08.

5-(4-Methoxyphenyl)-1*H*-tetrazole; (Entry 3, Table 4). White solid; m. p.: 232-234 °C; FT-IR(KBr, cm^{-1}): v 3225-2200 (N-H stretch.), 1608 (aromatic C=C stretch.), 1563 (N-H bending.), 1511 (C=N stretch.), 1405 (C-N stretch.), 1260 (N=N stretch.), 1189, 1111, 1021 (ring tetrazole and amine 2°.); ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 16.10 (br, 1H, -NH), 8.05-7.92 (d, 2H, J = 8.5 Hz, Ph), 7.16-7.13 (d, 2H, J = 8.5 Hz, Ph), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, δ (ppm)): 161.82 (NH-C=N), 154.55, 128.70, 116.43, 114.78, 55.63 (-OCH$_3$).

5-(3-Methoxyphenyl)-1*H*-tetrazole; (Entry 4, Table 4). White solid; m. p.: 157–158 °C. FT-IR (KBr, cm^{-1}): v 3302-2191 (N-H stretch.), 1605 (aromatic C=C stretch.), 1558 (N-H bending.), 1494 (C=N stretch.), 1414 (C-N stretch.), 1256 (N=N stretch.), 1153, 1102, 1008 (ring tetrazole and amine 2°); ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 16.93 (br, 1H, -NH), 7.66-7.62 (m, 1H, Ph),7.62-

7.58 (m, 1H, Ph), 7.60 (t, 1H, J = 8.08 Hz, Ph), 7.24 (ddd, 1H, J = 0.87, 2.50, 3.5 Hz, Ph), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, δ (ppm)): 160.02 (NH-C=N), 155.01, 130.7, 125.27, 119.04, 116.92. 112.1 (ph), 55.5 (-OCH_3).

5-Styryl-1*H*-tetrazole; (Entry 5, Table 4). White solid; m. p.: 156-158 °C; FT-IR (KBr, cm^{-1}): v 3250-2301 (N-H stretch.), 1600 (aromatic C=C stretch.), 1555 (N-H bending.), 1503 (C=N stretch.), 1400 (C-N stretch.), 1263 (N=N stretch.), 1182, 1089, 1010 (ring tetrazole and amine 2°), 758, 690; ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 15.95 (br, 1H, -NH), 7.85-7.50 (m, 5H), 7 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, δ (ppm)): 162.74 (NH-C=N), 135.01, 130.20, 128.36, 127.91, 126.59 (ph-C=C).

5-Benzyhydryl-1*H*-tetrazole; (Entry 6, Table 4). Yellowish; m. p.: 162-163 °C; FT-IR (KBr, cm^{-1}): v 3248-2275 (N-H stretch.), 1598 (aromatic C=C stretch.), 1558 (N-H bending.), 1491 (C=N stretch.), 1404 (C-N stretch.), 1275 (N=N stretch.), 1078, 1019, 936 (Ring tetrazole and amine 2°.) 803; ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 15.95 (br, 1H, -NH), 7.5-7.33 (m, 10H), 5.89 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, δ (ppm)): 160.23 (NH-C=N), 141.52, 129.03, 128.55, 126.29 , 45.18(PhCH).

5-(4-Bromophenyl)-1*H*-tetrazole; (Entry 7, Table 4). Yellow solid; m. p.: 266-267 °C; FT-IR (KBr, cm^{-1}): v 3158-2205 (N-H stretch.), 1600 (aromatic C=C stretch.), 1532 (N-H bending.), 1502 (C=N stretch.), 1430 (C-N stretch.), 1246 (N=N stretch.), 1176, 1067, 1013 (Ring tetrazole and amine 2°), 810; ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)) 17.02 (br, 1H, -NH), 7.93 (dd, 2H, J = 9.59 Hz, Ph), 7.87 (dd, 2H, J = 9.59 Hz, Ph); ^{13}C NMR (400 MHz, DMSO-d_6, δ (ppm)): 155.22 (NH-C=N), 132.61, 129.03, 124.85, 123.45.

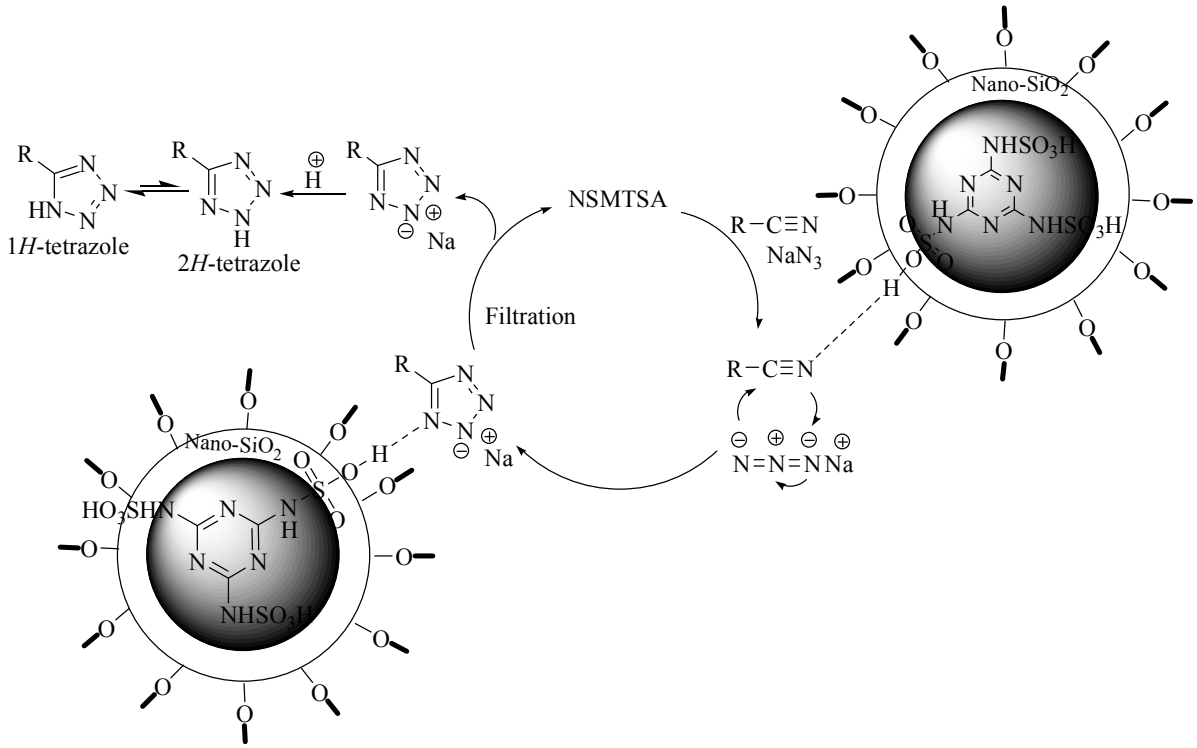
5-(4-Nitrophenyl)-1*H*-tetrazole; (Entry 8, Table 4). Yellow solid; m. p.: 221-222 °C; FT-IR (KBr, cm^{-1}): v 3147-2254 (N-H stretch.), 1601 (aromatic C=C stretch.), 1565 (N-H bending.), 1526 (-NO_2, Asym. stretch.), 1503 (C=N stretch.), 1417 (C-N stretch.), 1356 (-NO_2, Sym. stretch.), 1253 (N=N stretch.), 1160, 1095, 1018 (ring tetrazole and amine 2°), 812; ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 17.23 (br, 1H, -NH), 8.49 (dd, 2 H, J = 8.47 Hz, Ph), 8.33 (dd, 2H, J = 8.47 Hz, Ph).; ^{13}C NMR (100 MHz, DMSO-d_6, δ (ppm)): 155.87 (NH-C=N), 150, 131.87, 128.77, 124.41.

5-(4-Chlorophenyl)-1*H*-tetrazole; (Entry 9, Table 4). White solid; m. p.: 252-253 °C; FT-IR (KBr, cm^{-1}): *v* 3235-2366 (N-H stretch.), 1607 (aromatic C=C stretch.), 1533 (N-H bending.), 1485 (C=N stretch.), 1404 (C-N stretch.), 1253 (N=N stretch.), 1175, 1053, 994 (ring tetrazole and amine 2°), 800; ^{1}H NMR (400 MHz, DMSO-d_6 δ (ppm)): 17.09 (br, 1H, -NH), 8.10 (dd, 2H, *J* = 8.74 Hz, Ph), 7.68 (dd, 2H, *J* = 8.48 Hz, Ph).; ^{13}C NMR (100 MHz, DMSO-d_6, *δ* (ppm)): 155.65 (NH-C=N), 136.55, 130.16, 129.27, 124.01.

RESULTS AND DISCUSSION

To show the general capability of this method, a series of 5-substituted-1*H*-tetrazoles were prepared from various aromatic and aliphatic nitriles in the presence of NSMTSA as a heterogeneous mesoporous catalyst. All products were known compounds, identified by comparison of their spectral data (FT-IR, ^{1}H NMR, ^{13}C NMR) and melting points with those reported in the literature. The disappearance of the nitrile spots on the middle of TLC plate was a good primary sign for terminating the reaction. Furthermore, disappearance of a medium and sharp absorption band of CN stretching at 2150 cm^{-1} in addition to appearance of broad band at 2159-3235 cm^{-1} that is attributed to stretching absorption of NH bands and 1233-1293 cm^{-1} due to (-N-N=N-), 1041-1106 and 1110-1189 cm^{-1} due to tetrazole rings in IR spectra of products that were good characteristics of the formation 5-substituted-1*H*-tetrazoles. Furthermore, a ^{13}C NMR signal at 154-161 ppm is assigned to the quaternary carbon of NH-C=N.

Remarkably, the activity of nitrile compound toward azide ion plays an important role in [3+2] cycloaddition reactions. As shown in Table 3, in contrary to aromatic, aliphatic nitriles were reacted with sodium azide in shorter times and higher yields. The lower activity of aromatic nitilres may be attributed to their significant resonance between the aromatic ring and cyano group, which decreases its electrophilicity. In addition, aromatic compounds containing electron donating and withdrawing substituents at *para*- or *meta*-positions showed no significant difference in product yields or reaction times (Table 4, entries 1-9). This may be due to the strongly withdrawing effect of cyano group that the presences of other groups do not affect considerably on its behavior. Bifunctional aliphatic nitriles reacted similarly and provided good yields in formation of only one tetrazole ring (Table 4,



Scheme 3. A proposed mechanism for the preparation of 5-substituted-1*H*-tetrazoles in the presence of NSMTSA

entries 11-13).

On the basis of the triazole mechanisms, and tetrazole formation in the presence of acidic catalysts reported in literature, a plausible mechanism may be proposed (Scheme 3). It is hypothesized that, initially, coordination of acidic catalyst with nitrogen atom of nitrile compound is occurred. Rationally, this complexation will accelerate the cyclization process. This claim is supported by the experimental facts that the reaction was not proceeded remarkably in the absence of catalyst, even, after prolonged reaction time (Table 2, entry 1). After activation of cyano group by the NSMTSA, the [3+2] cyclization between the C≡N bond of nitrile compound and azideione could take place readily. Acidic workup will release the stable 5-substituted-1*H*-tetrazole (Scheme 3).

CONCLUSIONS

In summary, we have developed the application of NSMTSA nanocatalyst as an inexpensive, efficient, heterogeneous, and environmentally benign nanocatalyst for the facile synthesis of various tetrazoles in good to high yields. It is also notably emphasized that the catalyst was easily recovered and reused. It is envisaged that NSMTSA nanocatalyst is potentially applicable for a number of industrial scale production of 5-substituted-1*H*-tetrazoles.

ACKNOWLEDGMENTS

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